

VII.K.4 Advanced Catalysts with Reduced Noble Metal Content for Fuel Cells

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Projected End Date: Project continuation and direction determined annually by DOE

Objectives

- Develop new oxygen reduction catalysts that will contain substantially reduced amounts of precious or noble metals compared to state-of-the-art catalysts. Shift research focus from direct methanol fuel cell (DMFC) anode catalyst discovery (FY 2003 – 2004) to oxygen reduction catalysts.
- Demonstrate that optimized catalyst compositions can be implemented in practical fuel cells.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- B. Cost
- C. Electrode Performance

Technical Targets

Reduction in the use of noble metal catalysts with improved performance

- Near-term target of 2,000 mW/mg (or 0.25 mg/cm²) of noble metal based on the mass of noble metal.
- Improve cathode potential by 0.1 V over state-of-practice for current densities of >500 mA/cm²

Approach

- New non-noble, metal-based catalysts will be prepared using the co-sputter deposition methodology established in FYs 2003 and 2004.
- Develop a new electrochemical screening system that will allow for the simultaneous study of an array of oxygen reduction catalysts in the same solution bath.
- Fabricate electrode arrays with new oxygen reduction reaction (ORR) catalyst material compositions containing combinations of Pt, Ni, Zr, Co, Fe, Mo, Ti and other metals, and evaluate their electrochemical activity.
- Determine optimal compositions with minimal Pt content and demonstrate these catalyst compositions in a membrane-electrode assembly (MEA) in a full cell configuration.

Accomplishments to Date (first three months of project)

- Determined optimal Pt/Ru ratio for methanol oxidation to be 82/18 (atomic ratio) and demonstrated performance in an MEA configuration. Results showed good performance, demonstrating the potential of reducing loading substantially using the sputter deposition technique. These results demonstrated the validity of the technique of screening and the method of fabricating MEAs.
- Prepared powder NiZrPtRu DMFC anode catalyst with composition/microstructure similar to that of the material previously discovered using the thin-film, combinatorial method. Half-cell studies indicated that these materials deliver catalytic current densities approaching those of commercial Pt/Ru, and the materials displayed the expected high Pt-site usage. These results demonstrate that it is possible to translate the compositions discovered by sputter deposition to practical powder catalysts.
- Evaluated the effect of surface roughness of electrode substrates on MEA performance. Results suggest that substrate roughness can be exploited to improve thin-film catalyst-based MEA performance substantially.
- Designed, fabricated and tested a multi-electrode electrochemical test system for combinatorial screening of oxygen reduction activity of thin-film catalyst compositions. Preliminary results with pure platinum active areas show that the set-up will be useful in obtaining the necessary data for the planned course of research.

Future Directions

- Investigate new ORR catalyst materials consisting of combinations of two or more elements chosen from Pt, Ni, Zr, Co, Fe, Mo and Ti.
- Demonstrate performance of best catalysts in a membrane-electrode assembly in a full cell configuration.
- Use the results of composition and activity to develop a rationale for catalyst design.
- Perform lifetime testing of new catalyst materials.

Introduction

The previous two years of fuel cell catalyst research supported by the DOE at the Jet Propulsion Laboratory (JPL) focused on studying novel thin-film, corrosion-resistant, catalytic layers for DMFC anode application [1,2]. Over the course of this work, a methodology for combinatorially depositing multiple catalyst test coupons was developed, and a multi-channel electrochemical screening test station was built and implemented. Using this approach, several very promising materials combinations were isolated and showed excellent performance in a liquid solution half-cell test environment [3].

The focus of the ongoing FY 2005 effort is to transition this catalyst research methodology to the study of ORR cathode catalyst materials. Typically, very heavy loadings of Pt are used to facilitate the reaction, significantly impacting the overall fuel cell cost. The primary goal, then, is to find new ORR catalyst materials that have little or no Pt content yet

still have sufficient catalytic properties to be of practical use in fuel cells. Results of catalyst characterization will be used to develop an understanding of the effect of composition and microstructure on the performance of the catalysts. Such analysis will lead to a rational approach for catalyst design.

Before fully focusing on the cathode ORR chemistry, the efficacy of the experimental approach was studied with DMFC anode catalyst materials in a practical fuel cell environment. Also, powder catalysts were prepared based on the new non-noble metal containing compositions discovered using the combinatorial screening technique. The powder catalyst showed excellent performance similar to the thin-film catalysts. These experiments will support any future results using the combinatorial methodology, as the ability to transition new catalyst materials into practical and functional fuel cells is a critical element of this research.

Approach

New metal-based ORR catalysts with little or no noble metal content are to be prepared using a sputter co-deposition technique. These materials will be characterized using a multi-electrode combinatorial electrochemical polarization technique. The highest-performing catalyst materials will be incorporated into full hydrogen/air polymer electrolyte membrane (PEM) assemblies and tested. The effort is executed through three tasks:

- Task 1. Demonstrate approaches to transfer optimal sputter-deposited catalyst compositions to full cells
- Task 2. Develop a methodology for combinatorial electrochemical characterization of ORR catalysts
- Task 3. Prepare and evaluate new ORR catalysts

Results

Task 1: Demonstrate approaches to transfer optimal sputter-deposited catalyst compositions to full cells

This activity was conducted through three sub-tasks: 1) transfer compositions to MEAs by sputter deposition onto electrode structures, 2) prepare new powder catalysts by high-energy ball milling and determine performance, and 3) investigate the impact of substrate surface area on performance. The results of these efforts are described in the following.

DMFC MEAs with sputtered Pt₈₀Ru₂₀ catalyst layers

Previous results showed that the optimal surface composition of a Pt/Ru anode catalyst for a DMFC application is 82/18 Pt/Ru [3]. To further test this finding, a full MEA was fabricated using a uniform thin film of Pt₈₂Ru₁₈ deposited directly on a Toray paper anode current collector and integrated into to a Nafion[®]-based PEM fuel cell. Figure 1 compares the performance of such an MEA with that of a conventional MEA with a high catalyst loading. Though the sputtered surface did not out-perform the conventional material when normalized to MEA area, the catalyst usage of the sputtered layer was over an order of magnitude greater than that for the powder-based material. With about 1/80th the

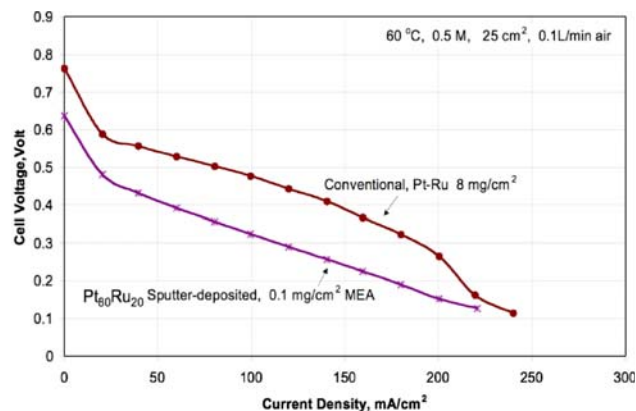


Figure 1. Performance of conventional MEA using 8 mg/cm² Pt/Ru anode catalyst powder compared with optimized sputter-deposited Pt₈₂Ru₁₈ thin film with a loading of 0.1 mg/cm². The current density values were normalized to total electrode area.

amount of catalyst, the performance of the MEA with the sputtered catalyst was about a third of the performance of the conventional MEAs. It should be noted that the test conditions used for this testing—60°C, 0.1 L/min air flow—were colder and used lower air flow than compared to the conditions used in other published results from thin-film catalyst layers, and are more representative of nominal DMFC operating conditions. Furthermore, the surface area of the commercial powder catalyst used in the conventional MEA was much greater than that of the sputtered film. Therefore, enhancement of the surface area of the sputtered film will lead to even better overall MEA performance.

NiZrPtRu powder catalysts

A promising DMFC anode catalyst composition of Ni₃₀Zr₁₃Pt₃₃Ru₂₃ was derived from investigation of sputter-deposited catalyst layers in the FY 2004 effort. To make this catalyst amenable to conventional processing and eventual insertion into industrial MEA fabrication, a powder form factor is desired. Therefore, through an informal collaboration with Prof. Kumta of Carnegie Mellon University (CMU), powder materials based on this new composition were prepared. High-energy ball milling, also known as mechanical alloying (MA), was selected as a fabrication route because powders fabricated this way are likely to possess nanocrystalline and/or meta-stable phases similar to

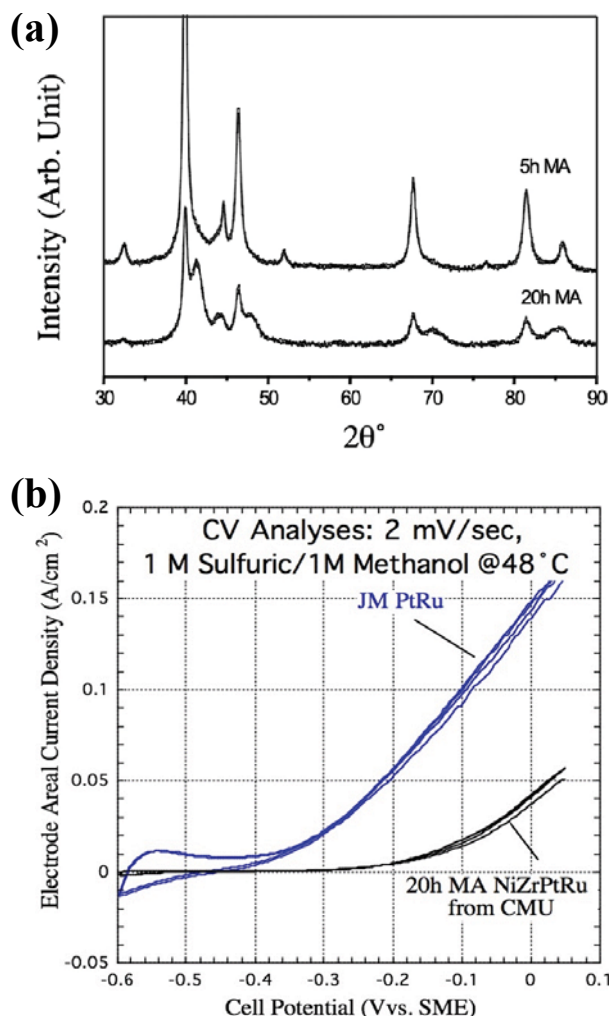


Figure 2. (a) X-ray diffraction from NiZrPtRu materials as mechanically alloyed for 5 and 20 hours. The 20 h powder had significantly smaller grains and a defined nanophase content compared to the material milled for 5 hours. (b) Cyclic voltammetry on the 20 h mechanically-alloyed NiZrPtRu as compared to commercial (Johnson Matthey) Pt/Ru powder. The reference electrode used was Mercury Sulfate Electrode (SME), which is 0.650 V positive to the normal hydrogen electrode (NHE).

those found in our sputtered NiZrPtRu films. Figure 2 shows results from x-ray diffraction analysis of NiZrPtRu after MA for 5 and 20 hours.

After 20 hours of MA processing, the NiZrPtRu contained a significant mass fraction of a nanophase

alloy with average grain sizes of less than 10 nm (as indicated by the broad peaks found around 2θ values of 43° , 70° , and 85°). Cyclic voltammetry of the 20-hour MA powder was promising; current densities were observed that were one-third to one-tenth of those found in a high-surface-area commercial PtRu powder. Preliminary BET (Bruner, Emmett and Teller) surface analysis of the MA powders conducted at CMU indicated that these powders had less than 1/10 the surface area of the commercial Pt/Ru powder catalysts. Thus, normalization of the polarization data to actual catalyst surface area would show that the NiZrPtRu had comparable performance to the high-Pt-content Pt/Ru.

Investigating the effect of substrate surface area

In both of the studies described above, the rationale given to explain the limited performance (as normalized to functional MEA area) associated with new catalyst layers was that a lower catalytic surface area was present in the new test materials compared to the high-surface-area commercial powders. Therefore, an experiment was conducted to probe the significance of the surface area effect in the thin-film catalyst system. An optimized $Pt_{82}Ru_{18}$ film was deposited simultaneously onto two substrates with different morphologies: carbon Toray paper and a polished Si wafer. Subsequent electrochemical analyses showed that the film deposited on the rough Toray paper yielded about eight times the current density compared to the same film on the smooth substrate under identical half-cell test conditions. Figure 3 shows these results.

First-order calculations (based on morphology observed using scanning electron microscopy, SEM, as seen in Figure 3) indicate that the Toray paper is between 5 and 10 times rougher than the silicon substrate, a finding consistent with the conclusion that catalytic current density scales linearly with catalyst-electrolyte surface area. This preliminary result supports the previous assertion that surface area is critical to assessing catalyst performance. Thus, the novel catalyst compositions that have been developed in this project to date are likely to be at least as active as the commercial Pt/Ru baseline when normalized to actual catalyst surface area.

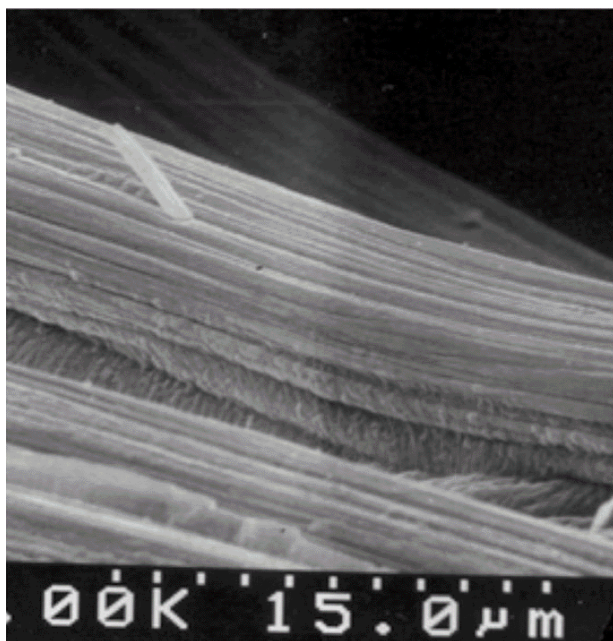
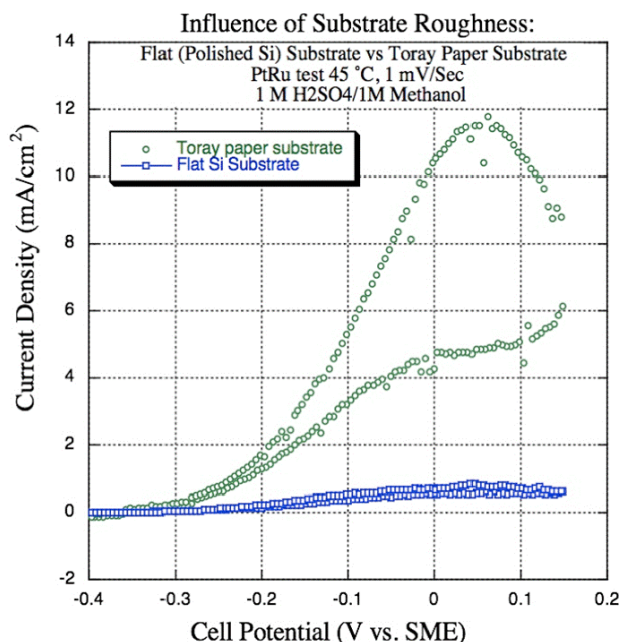


Figure 3. (top) Cyclic voltammetry of identical Pt₈₂Ru₁₈ thin films deposited onto a rough carbon Toray paper substrate and a polished Si wafer. The average current density observed from the Toray substrate film increased by a factor of approximately 8 for cell potentials greater than -0.2 V vs. SME (0.45 V vs. NHE). (bottom) SEM image of a strand of Toray fiber.

Task 2: Develop a methodology for combinatorial electrochemical characterization of ORR catalyst

To extend the experimental methods developed originally for DMFC anode catalyst materials, a new approach to screening multiple ORR catalyst materials in a single solution bath was needed. Commonly, a rotating-disc electrode is used. This configuration, however, precludes the use of multiple electrodes, which is a necessary aspect of the previously developed combinatorial screening system. To use a combinatorial electrode array, an arrangement that involves rotation of the electrolyte solution fluid instead of the electrodes to produce similar laminar flow at each active area was developed. The laminar fluid flow conditions found on the perimeter of a large-diameter cylindrical bath that is stirred at a high rate were used. Under these conditions, oxygenated electrolyte solution flows past the multi-electrode array in a uniform fashion, presenting each electrode with a similar dissolved oxygen content. Such an electrode array is deposited onto a flexible polyvinylidene fluoride (PVDF) substrate and held against the walls of the cylinder (Figure 4). Preliminary tests to verify materials and geometry functionality were conducted on PVDF/Au substrate/current collector structures with 1 cm² Pt active areas.

Figure 5 shows potentiodynamic scans of a 6-electrode Au current collector/Pt active area sample-set in a 1 M H₂SO₄ solution. With a constant Ar bubble, the electrodes delivered nearly identical current densities through the potential range studied (Figure 5a), showing that the multi-channel pseudo potentiostat was functioning properly.

Potentiodynamic scans of the same electrode array after oxygenation of the electrolyte showed that the ORR took place at the expected onset potential of about 0.85 V vs. NHE, as seen in Figure 5(b). At lower cell potentials, the data became more dispersed as a result of reaching the mass-transport-limited regime of the reaction. These data may be averaged to give meaningful results, as shown in Figure 6.

In this case, there is a clear dispersion between the electrodes as a function of position at lower electrode potentials. Since the oxygen in the solution was exposed to cell 6 first (followed by 5, then 4,

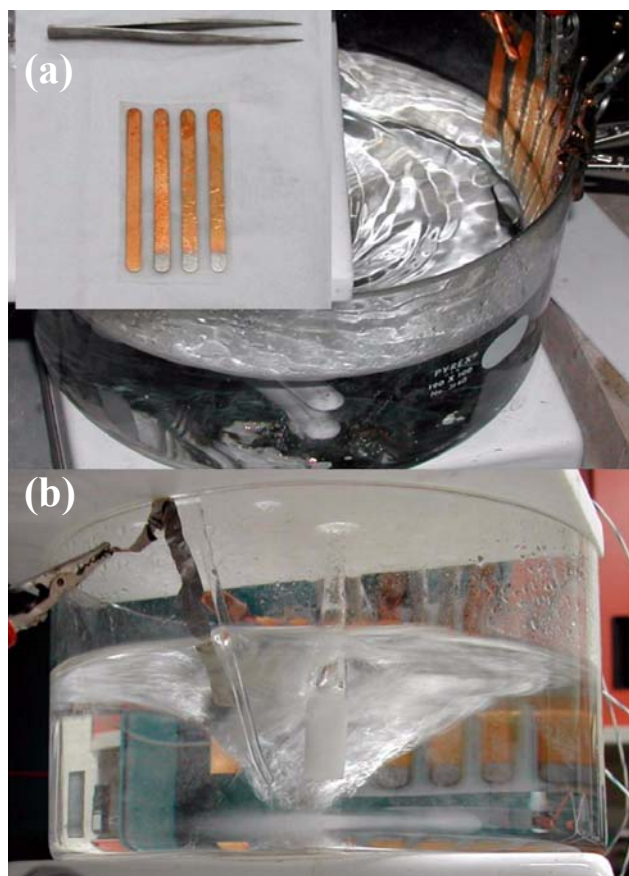


Figure 4. (a) Image of Au current collector with 1 cm^2 Pt active area test structure (inset), top view of stirred test bath. (b) Side view of stirred solution test bath showing Pt counter electrode, SME reference electrode, oxygen bubbler, and test coupon.

etc.), the observed lower current densities are likely a result of the depletion of the oxygen in the laminar layer of the solution as it passes over the electrodes under test. This effect is currently under study, and methods to eliminate or minimize it are under development.

Task 3. Prepare and evaluate new ORR catalysts (ongoing task)

Multi-component metallic materials will be prepared as thin films. This task involves first selecting the mix and range of candidate metals, followed by actually preparing multi-component materials. Potential catalytic activity and corrosion stability of the multi-component materials are important criteria that will be used in the selection of materials. Non-noble metals with unfilled d-bands

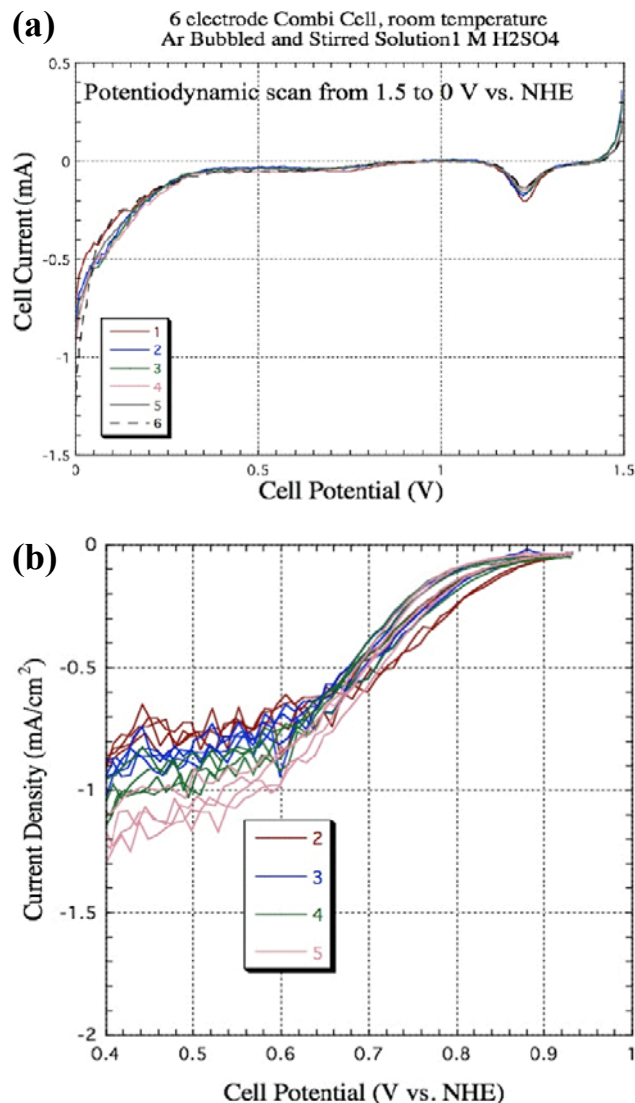


Figure 5. (a) Potentiodynamic scan on a six-electrode array from 1.5 to 0 V vs. NHE in stirred 1 M H_2SO_4 solution with bubbling Ar. These raw data show virtually identical signals from the 6 electrodes. (b) Same test conditions but with O_2 bubble (before smoothing).

are catalytically active for dehydrogenation reactions. However, in order to realize good catalytic activity, the heat of adsorption for the surface intermediates should be neither too large nor too small [4]. Such an optimal interaction can be achieved only by tuning electronic states of the metal using a second element. A combination of two or more transition metals with widely varying d-electron configuration gives rise to significant electronic interaction between the metals [5]. By combining the metals in appropriate ratios, the work

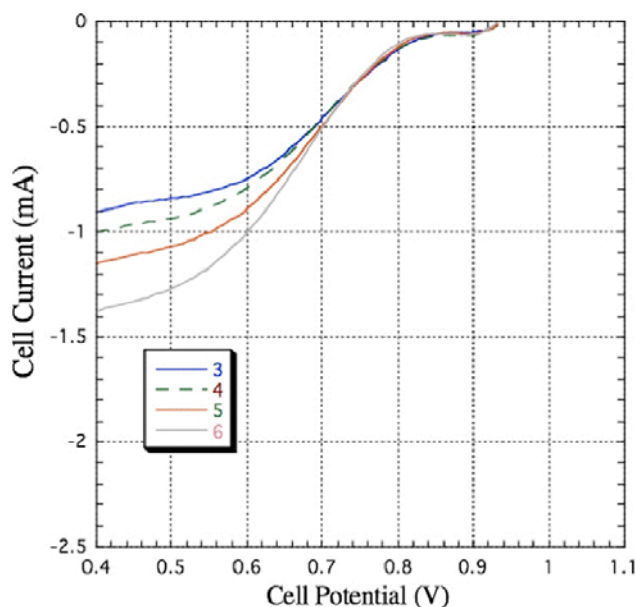


Figure 6. Smoothed ORR data collected at room temperature for electrodes 3 through 6. The data show gradual depletion of the oxygen in the laminar layer as it flows from 6 to 3. The potential range of interest for screening purposes occurs where the initial onset of the catalytic reaction takes place, in this case in the range $0.7 < V < 0.9$. In this range, the Pt electrodes give identical data, as expected.

function of the constituents of the inter-metallic can be tuned [6]. Such work function changes can be of the order of 1-2 eV. This magnitude of energy change is comparable to the changes in the heat of chemisorption calculated for various metals [7]. In this effort, non-noble metal combinations involving Ni and Co will be investigated. Initial screening will be based on the expected shift in work functions, alloying tendencies and relative mobilities in the lattice. The foregoing elements will be combined with small amounts of platinum and ruthenium to generate multi-component systems.

To be useful as fuel cell catalysts, these multi-component systems must be corrosion-resistant in strongly acidic environments. Such corrosion resistance can be achieved by including metals such as zirconium in the multi-component system. Zirconium offers corrosion protection by forming oxide films that resist dissolution of the metals in acid. To this end, we will be focusing on XYNiZr films, where X and Y could be Pt, Ni, Ru, Co, Fe, Mo, or Ti.

Conclusions

- Materials optimized using the novel combinatorial selection methodology were demonstrated in practical fuel cells.
- Mechanical alloying was used to fabricate powders of combinatorially selected materials. These powders demonstrated promising performance when tested in a half-cell environment.
- A preliminary study on the effects of catalyst surface area on the performance of the MEA was conducted using identical thin-film Pt/Ru catalyst layers on different substrates. These results are consistent with the conclusion that some of the new catalyst materials could be competitive with traditional catalysts if prepared with high surface area.
- A new method for electrochemically screening ORR catalysts has been developed. In this approach, multiple (up to 36) different catalyst test coupons may be tested at the same time.
- The sputter deposition method and combinatorial screening technique will be extended to the development and discovery of new catalysts for ORR.

Special Recognitions & Awards/Patents Issued

1. Patent Pending, May 2005: "A Low Pt Content Direct Methanol Fuel Cell Anode Catalyst: Nanophase PtRuNiZr"

FY 2005 Presentations

1. "Low Pt Content DMFC Catalyst Discovery Using Combinatorially-Deposited Nanoscale Thin Films." Electrochemical Society Fall 2004 Meeting, October 2004, Symposium W1 - Fourth International Symposium on Proton Conducting Membrane Fuel Cells, Talk #1898

FY 2005 Publications

1. *Investigation of Direct Methanol Fuel Cell Electrocatalysts Using a Robust Combinatorial Technique*, Jay F. Whitacre, T. Valdez, and S. R. Narayanan, Journal of The Electrochemical Society, 152 9 A1780-A1789 2005

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